

A point-to-point response and relevant changes made in the revised manuscript

Anonymous Referee #1

Manuscript entitled “Chemical characterization of organic compounds involved in iodine-initiated new particle formation from coastal macro-algal emission” studied the identity and transformation mechanisms of organic compounds from low-tide macroalgal emission. This manuscript simulates vapor emission oxidation and new particle formation (NPF) experiments of real coastal macroalgae in a bag-reactor. Based on the integrated mass spectrometry measurements, the authors report for the first time a variety of volatile precursors and their oxidation products in the gas and particle phases in such a highly complex system. The results show that organic compounds dominate the growth of new particles induced by iodine species.

This paper falls in an active field of research, and I believe it brings interesting insights to the study of the ongoing laboratory and field researches of coastal I-NPF. The paper could be published in the journal assuming some minor corrections.

Re: We thank the referee for careful examination and important comments of the manuscript. Point-to-point responses were given below. Changes were made in the revised manuscript accordingly.

Comments

Page 4 Lines 96-98: What is the proportion of VOCs and O₃ in the VOCs/O₃ flow of the dynamic mode, respectively?

Re: we used the vapor mixture emitted from macroalgae in the experiment. As one can see, there are many VOC species in the mixture. Unlike those studies focusing on a single precursor, it is not possible for us to estimate the ratio of VOCs and O₃. The purpose of this study is to qualitatively measure the oxidation products of algae-emitted VOCs in the simulated NPF event.

Page 4 Lines 98-99: Does the residence time of 67min refer to the sampling time of particulate matter?

Re: No, residence time is reaction time in the bag reactor, which is the volume of bag reactor divided by the flow rate of VOCs/O₃ flow. Now we add in line 103-104:

“The bag reactor was then operated in a dynamic mode for a few hours to collect enough particles for offline chemical analysis.”

Page 5 Lines 133-134: How can we see from Figure 2a when O₃ is injected? And when to add light? Why only see the figure of SMPS under static conditions of the ozonolysis experiment.

Re: our pilot study showed that no particles formed in the absence of room light or O₃. Therefore, O₃ and light were supplied throughout the experiments of chemical characterization. Even in the first 48 minutes after O₃ were added, we could not observe any particle or gas-phase product. So we

did not show the data during that early period. Time zero of Figure 2 was set as the time when gaseous products first appeared.

In the dynamic condition of the experiments, continuous time evolution of particle size can not be measured. So we did not show SMPS particle size spectrum. The particle size at the outlet of the bag reactor was shown in Table 2.

Now we add the following description in line 142-147:

“No particles formed in the absence of room light or O₃. Therefore, light was on throughout the experiments reported in the article. In the static mode experiments, we could not observe gas-phase products until 48 minutes after O₃ injection. New particles larger than 14 nm were observed only 58 minutes after O₃ injection. Afterwards, new particles begun to grow to form a typical banana-shape particle size spectrum (Figure 2a). This relatively long waiting time was likely due to the build-up of O₃ and oxidation products. Time zero of Figure 2 was thus set as the time when gaseous products first appeared.”

Page 5 Line 157: Please indicate what kind of macroalgae you choose and how to preserve the algae and seawater. And why you choose this type of macroalgae?

Re: we have the description in line 77-78:

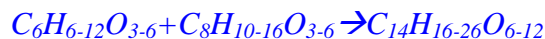
“Undaria pinnatifida, a common brown seaweed species at Xiangshan gulf of east China coast, was collected from local intertidal zone and stored at -10°C until the experiments.”

Page 8 Lines 225-229: Does accretion reactions or dimer formation change particle size? Please describe the accretion reaction in detail.

Re: As one can see in Figure 2a, new particles kept on growing to form a typical banana-shape particle size spectrum. However, we can not differentiate, by our experiment, the growth was due to the uptake of gaseous products or accretion reactions in the particles. In theory, accretion reaction, by itself, should not brought new mass to the particles.

We described the accretion reactions in line 284-298:

“For such a highly complex system full of various algae-emitted precursors, it is impossible to simply propose a reaction mechanism to explain the formation of all particulate products, nor to list all reactions occurring in the bag reactor. On the basis of particle-phase oligomer chemistry (Seinfeld and Pandis, 2016), especially the well-understood isoprene ozonolysis SOA chemistry (Nguyen et al., 2010; Inomata et al., 2014; Riva et al., 2017), we suggest a variety of accretion reactions without uniform oligomerization pattern (e.g., esterification, aldol condensation, hemiacetal reactions, peroxyhemiacetal formation and SCI reactions, etc.) transformed $O_{max}=4$ and $C_{max}=8$ multifunctional monomers (like alcohols, carbonyls, hydroperoxides, carboxylic acids) to $O_{max}=8$ and $C_{max}=14$ or 16 dimers. As an example, we used the following two reaction equations to illustrate addition type cross-oligomerization between C_6 and C_8 monomers and self-oligomerization of C_8 monomers, respectively:



in which the C₆, C₈, C₁₄ and C₁₆ formulas in the equations are among the most abundant ones observed in the particle phase by the iodide-CIMS.”

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Page 8 Lines 230-232: Why do ESI-Orbitrap MS and FIGAERO-iodide-CIMS use quartz fiber filter and PTFE membrane filter, respectively? Is filter inconsistency the reason why ESI-Orbitrap MS did not measure bimodal distribution?

Re: PTFE membrane filter is the recommended for particle collection and thermal desorption in FIGAERO. Its relative large pore size avoids excessive pressure drop across the filter during the sampling. Quartz fiber filter was used for ESI-orbitrap MS, total iodine and total organic carbon measurements. The advantage of quartz filter is that background contaminants on the filter could be removed using thermal combustion prior to particle collection.

Chemical composition difference observed by ESI-Orbitrap MS and FIGAERO-iodide-CIMS might resulted from many factors, like sample substrate, extraction method, ionization mechanism and MS resolution. Systematic investigation of the effect of these factors is out of scope of this manuscript. The motivation of performing ESI-Orbitrap MS analysis in our work is to facilitate the comparison with isoprene and alpha-pinene ozonolysis products reported by prior ESI-Orbitrap MS measurements in the literature. From our experience, we believe ionization mechanism (ESI vs. I⁻ clustering) might be the most important factor.